(24) 29.9.80

- (54) GOLD AND SILVER RECOVERY
- (71) DEXTEC METALLURGICAL PTY. LTD.
- (87) WO 82/01195 (21) 75848/81 545429
- (22) 18.9.81
- (43) 3.6.82 (44) 11.7.85

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- $(51)^3$  C228 11/04 C228 11/06
- (72) P.K. EVERETT
- (74) CM
- (56) 23613/70 453463 14.3 49153/64 14.3
- (57) Claim
  - 1. A process for the recovery of silver from a silver bearing ore or concentrate which comprises:
  - (a) forming a mixture of ore or concentrate and a strong electrolyte containing sufficient chloride ions to form a complex with the silver,
  - (b) maintaining the mixture at a temperature up to the boiling point of the electrolyte,
  - (c) maintaining the pH of the mixture above 2, whereby silver is taken into solution; and
  - (d) contacting the solution with metallic iron or steel to precipitate the silver from the solution.
  - 2. A process for the recovery of gold from gold bearing ore or concentrate which comprises:
  - (a) forming a mixture of ore or concentrate and a strong electrolyte containing sufficient chloride ions to form a complex with the gold,
  - (b) maintaining the mixture at a temperature up to the boiling point of the electrolyte,
    - (c) maintaining the pH of the mixture above 4,

.../2

includes:

whereby the gold is taken into solution; and

- (d) contacting the solution with a metal in the electrochemical series having a potential above that of the gold to precipitate the gold from the solution.
  15. A process for the recovery of silver and gold from a silver and gold bearing ore or concentrate which
- (a) forming a mixture of ore or concentrate and a strong electrolyte containing sufficient chloride ions to form a complex with the silver and gold,
- (b) maintaining the mixture at a temperature up to the boiling point of the electrolyte,
- (c) maintaining the mixture at a pH sufficient to selectively take silver into solution,
- (d) contacting the solution with a metal having a potential above salver in the electrochemical series to thereby precipitate silver from the solution,
- (e) adjusting the pH of said solution to a level whereby gold is taken into said solution, and
- (f) contacting the solution with a metal having a potential above gold in the electrochemical series to precipitate gold from the solution.

THOMSON & CARTER Patent Attorneys

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# Declaration in Support of an Application for a Patent

(Combined Form - Convention and Non-Convention)

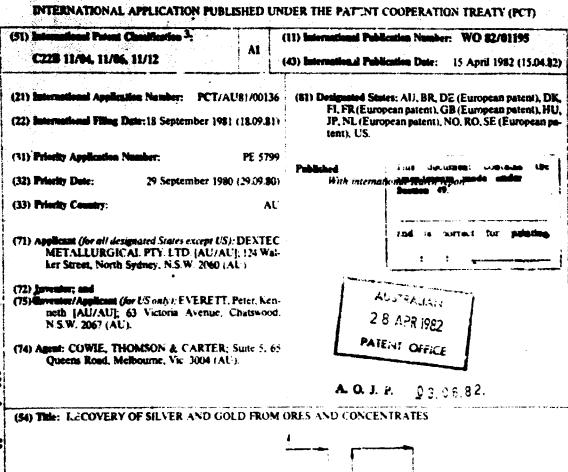
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	Peter K. Everett Director, of						
	Dextec Metallurgical Pty. Ltd.						
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	do solemnly and sincerely declare as follows:-						
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••••	(or in the case of an application by a body corporate)						
	1. I am authorised by Dextec Metallurgical Pty. Ltd.						
	the applicant for the patenticological to make this declaration on its behalf.						
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	the actual inventor(8) of the invention and the facts upon which XXXIII the						
	said company is entitled to make the application are as follows:-						
	The said company is the assignee of the invention from the said actual inventor.						
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	application(s)-made in a Convention country in respect of the invention the subject of the						
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	May, 1984						
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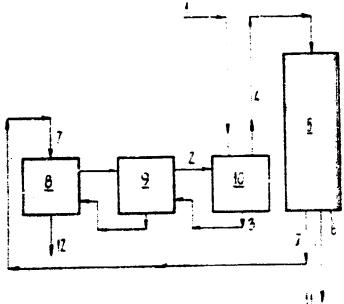
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### PCT

# WORLD INTELLECTUAL PROPERTY ORGANIZATION





(57) Abstract

Silver and/or gold (12) are recovered from ores or concentrates (1 m) forming a mixture of the ore or concentrate (1) with electrolyte contaming chloride ions (2) and maintaining the mixture at a temperature up to the boiling point of the electrolyte (2) whereby the silver and/or gold (12) is taken into solution (4). The gold and/or silver (12) is precipitated from the solution (4) by contacting the same with a metal having a potential higher than gold or silver in the electrochemical sense. If gold is required the pH of the volution is adjusted to greater than 4.

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FIELD OF THE INVENTION 3 4 5 4 2 9

BACKGROUND OF THE INVENTION

This invention relates to a hydrometallurgical method of recovering silver and/or gold from ores and concentrates.

Silver and gold are produced in major quantities as by-products from the smelting of ores and concentrates to produce metals such as copper and lead. In general these smelting methods are not used to treat ores containing small amounts of silver without appreciable quantities of copper and lead etc. which are normally required to make the process economic.

Typically low grade silver ores are treated by flotation and cyanidation. However this can result in low recoveries due to the variety of mineralisation which may be present. An example of this type of mineralisation is the very large mainly low grade silver deposits near Barstow in California, U.S.A. Using conventional techniques only approximately 50% recovery of the contained silver could be achieved from most samples.

In handling very large tonnages of mainly low grade ore, the processing costs are extremely important as even such steps as heating the ore, or use of reagents, pressure, or specialised equipment, can quickly render a process uneconomic.

#### DESCRIPTION OF THE PRIOR ART

In U.S. Patent 4,131,454 (Piret et al 1978) there is described a method of selectively separating Au and Ag from solution using activated carbon and iodide from chloride solutions. Iodide can be expensive, and the formation of silver iodide leads to the incorporation of further processing steps to produce metallic silver.

In U.S. Patent 4,127,639 (Piret et al 1978) there is described the selective separation of lead and silver from chloride solutions using sulphide e.g. H<sub>2</sub>S. As is the

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case with U.S. Patent 4,124,454 further processing steps are necessary to convert the silver sulphide to metal.

In U.S. Patent 4,124,379 (Piret et al 1978) there is described a method of precipitating silver as an amalgam. Again further processing is necessary to finalize the recovery of silver.

In U.S. Patent 4,113,471 (Langhurst et al 1978) there is described the dissolution of silver in chloride solution at pressures of 200 - 600 pounds per square inch, and temperatures between 125°C and 225°C. This process consequently requires use of expensive equipment and closecontrol of operating parameters.

In U.S. Patent 4,110,109 (Golben 1978) there are described methods of improving the precipitation of silver on steel wool by inhibiting a side reaction. This side .... reaction consists of a hydrogen ion attack on the steel wool.

In U.S. Patent 4,035,181 (Fisch 1977) there are described further methods of reducing hydrogen ion attack & steel wool during silver precipitation.

In U.S. Patent 3,774,995 (MacKay 1973) there is described an apparatus for cementation of silver from photographic solutions onto a woven mesh screen. The apparatus suffers from being expensive which, as will be appreciated from the preceding comments, affects the viability of a process.

In U.S. Patent 3,369,801 (Hartman 1968) there is described another relatively expensive apparatus for the use of material, such as steel wool, for cementation of silver from photographic solutions.

In U.S. Patent 410,961 (Lyte 1879) there is described the dissolution of metals in chloride solutions and the precipitation of silver on lead, which is stated to be "far superior to iron, copper or any other metals, the employment of which may have been proposed for collecting silver from its solutions".

The object of this invention is to provide a low cost process which results in very high recoveries of high

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grade silver using simple inexpensive equipment whilst avoiding the formation of dangerous pollutants. The conditions of the process can be adjusted to recover silver, silver and gold, or just gold, depending on the amounts of the two metals present in the ore or concentrate to be treated.

#### THE INVENTION

The process of this invention overcomes the disadvantages of the above processes and provides a low cost method of recovering silver and/or gold from a variety of minerals by dissolving the metal in a low cost electrolyte followed by a simple inexpensive recovery procedure to produce a high grade silver and/or gold product. The process of the invention avoids the build up of foreign ions in solution which otherwise would require periodic replacement and/or treatment to remove excess ions.

According to one aspect of the invention there is provided a process for the recovery of silver from a silver bearing ore or concentrate which comprises:

- (a) forming a mixture of ore or concentrate and a strong electrolyte containing sufficient chloride ions to form a complex with the silver,
- (b) maintaining the mixture at a temperature up to the boiling point of the electrolyte,
- (c) maintaining the pH of the mixture above 2, whereby silver is taken into solution; and
- (d) contacting the solution with metallic iron or steel to precipitate the silver from the solution.

According to another aspect of the invention there is provided a process for the recovery of gold from gold bearing ore or concentrate which comprises:

- (a) forming a mixture or ore or concentrate and a strong electrolyte containing sufficient chloride ions to form a complex with the gold,
- (b) maintaining the mixture at a temperature up to the boiling point of the electrolyte,

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- (c) maintaining the pH of the mixture above 4, whereby the gold is taken into solution; and
- (d) contacting the solution with a metal in the electrochemical series having a potential above that of the gold to precipitate the gold from the solution.

According to a further aspect of the invention there is provided a process for the recovery of silver and gold from a silver and gold bearing ore or concentrate which includes:

- (a) forming a mixture of ore or concentrate and a strong electrolyte containing sufficient chloride ions to form a complex with the silver and gold,
- (b) maintaining the mixture at a temperature up to the boiling point of the electrolyte,
- (c) maintaining the mixture at a pH sufficient to selectively take silver into solution,
- (d) contacting the solution with a metal having a potential above silver in the electrochemical series to thereby precipitate silver from the solution,
- (e) adjusting the pH of said solution to a level whereby gold is taken into said solution, and
- (f) contacting the solution with a metal having a potential above gold in the electrochemical series to precipitate gold from the solution.

A common method of separation of ionic silver from solution is precipitation as a chloride: Ag+ Cl → AgCl. The silver chloride, however, is soluble in excess chloride with the formation of a strong Ag/Cl complex. With the present invention it is possible to quickly and efficiently extract silver from many ores and concentrates at low temperatures, (e.g. 20 - 30°C) and low acid conditions

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grade silver using simple inexpensive equipment whilst avoiding the formation of dangerous pollutants. The conditions of the process can be adjusted to also recover gold.

#### 5 THE INVENTION.

The process of this invention overcomes the disadvantages of the above processes and provides a low cost method of dissolving precious metal from a variety of minerals, in a low cost electrolyte followed by a simple inexpensive recovery procedure to produce a high grade precious metal product. The method avoids the build up of foreign ions in solution.

The term "precious metal" used herein means "silver and/or gold".

Accordingly there is provided a process for the recovery of precious metal from a precious metal bearing ore or concentrate which includes:

- forming a mixture of ore or concentrate and an electrolyte containing chloride ions and maintaining the mixture at a temperature up to the boiling point of the electrolyte whereby the precious metal is taken into solution; and
- 2) precipitating the precious metal from said solution by contacting same with a metal having a potential above that of the precious metal in the electrochemical series. If gold recovery is required, the pH of the solution is adjusted to greater than 4 and preferably greater than 7 to allow dissolution of the gold, which may be recovered separately, or with the silver.

A common method of separation of ionic silver from solution is precipitation as a chloride: Ag<sup>+</sup> + Cl<sup>-</sup> → AgCl. The silver chloride, however, is soluble in excess chloride with the formation of a strong Ag/Cl complex. With the present invention it is possible to quickly and efficiently extract silver from many ores and concentrates at low temperatures, (e.g. 20 - 30°C) and low acid conditions

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using a high strength chloride solution to promote the formation of this complex. In addition, the silver recovery from solution using the method stated does not result in a build up of foreign ions in solution, which would normally require periodic replacement of the solution. The strong complex formed by the silver in the strong chloride solution is believed to assist in the oxidation of silver minerals by lowering the oxidation potential required.

The oxidation of gold is also assisted by the strong chloride solution as shown by the following potentials.

$$Au \longrightarrow Au^{+++} + 3e$$
  $E^{\circ} = -1.50$   
 $4Cl^{-} + Au \longrightarrow AuCl_{4}^{-} + 3e$   $E^{\circ} = -1.00$ 

The silver minerals treated by this process may be classified as those not requiring oxidation, those requiring a mild oxidising agent, and those requiring a strong oxidant. Since other oxidisable material may be present with the silver mineral, it may be important to use the lowest cost oxidising agent possible. If gold is present, recovery will normally require the use of a strong oxidant such as chlorine or hypochlorite ion and a pH above about 4. The silver and gold are then recovered from solution by methods such as cementation on a metal above silver and gold in the electromotive series. If desired, the silver may be leached first (e.g. at a pH of less than about 4, preferably 2.5) and the silver removed from solution before the pH is raised to effect leaching of gold, thereby allowing separate recovery of the silver and gold.

## 30 PREFERRED ASPECTS OF THE INVENTION

A preferred method for recovery of the silver and gold from solution is by cementation on iron or steel particles. During the precipitation stage iron is liberated into the solution according to:

$$2Ag^{+} + Fe^{0} \longrightarrow Fe^{++} + 2Ag^{0}$$

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Typically the leach stage is conducted at a pH above 2 and preferably above 3, and when electrolyte from the mineral recovery stage is reused in the leach, the iron is precipitated as hydrated ferric oxide or other oxide forms. If air is used as the oxidant, the iron may precipitate according to:

$$2Fe^{++} + 2H_2O + \frac{1}{2}O_2 \longrightarrow Fe_2O_3 + 4H^+$$
 (2)

or

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$$2\text{Fe}^{++} + \frac{1}{2}\text{O}_2 + 3\text{H}_2\text{O} \longrightarrow 2\text{FeOOH} + 4\text{H}^+$$

10 If silver is being leached according to:

$$4Ag + O_2 + 4H^+C1^- \longrightarrow 4Ag^+C1^- + 2H_2O$$
 (3)

the hydrogen ions are consumed and there is no build up in the electrolyte which would be expensive, requiring periodic replacement or treatment of the electrolyte. The overall reaction is the sum of the equations (1), (2) and (3) which when balanced give  $2\text{Fe} + 1.50_2 \longrightarrow \text{Fe}_2\text{O}_3$ .

i.e. silver is leached and precipitated (as is iron) and the electrolyte is continuously replenished. To facilitate the air oxidation and dissolution of some silver ores, the use of an ionic copper catalyst has been found advantageous. This element often accompanies silver mineralisation or is readily available.

The following examples show the dissolution of some silver minerals in concentrated chloride solution, under varying oxidising conditions.

#### Example 1.

An electrolyte (700 mls) containing 200 gpl of sodium chlor.de was slurried with 70 g of oxidised silver ore from the Barstow deposit containing 120 ppm silver. The slurry was aerated at pH 3.5 for 2 hours at 30°C. The residue contained 8 ppm silver indicating a recovery of greater than 90%.

Example 2.

A more resistant silver ore containing 550 ppm

35 silver was slurried with an electrolyte containing 250 gpl



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of sodium chloride. The slurry was aerated at ph 3.5 for 2 hours at 30°C. The residue contained 250 ppm silver indicating a 55% recovery.

#### Example 3.

The test of example 2 was repeated with 200 ppm of ionic copper in the solution. The residue contained 6 ppm silver indicating a 99% recovery.

#### Example 4.

A feed material of 85 ppm silver was aerated in sodium chloride (25%) in the presence of ionic copper at a.... pH of 3.5 for 4 hours at 30°C. The residue contained 30 .... ppm silver. This material was then leached in 25% sodium chloride solution at pH 3.5 with the addition of chlorine gas sufficient to maintain a positive starc. iodide test. The residue contained 2 ppm silver indicating an overall .... 97% recovery. The aeration step is carried out before the chlorine step to prevent wastage of chlorine on readily oxidised minerals.

#### Example 5.

The following table shows the dissolution of gold in a sodium chloride electrolyte at pH's between 3 and 8.

Feed: 7.8 ppm Au

Slurry Density: 30% /,

Oxidant : Chlorine to maintain positive

starch iodide test.

Temperature : 30°C

Time : 4 Hours

pH : 3.0 4.0 5.0 6.5 8.0 Residue Au ppm : 6.5 6.0 0.5 0.3 0.5

#### 30 Example 6.

The following results illustrate the precipitation of silver from a chloride solution using finely divided iron.

Temperature : Room approximately 18°C

35 Weight iron : 0.2 g

Electrolyte : 700 mls of 110 ppm silver in 20%

NaCl

рH : 2.5



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	Time (Hrs.)		ppm Ag.	ppm Fe.
	0		110	3
	0.25		110	19
	0.5		80	29
5	0.75		50	38
J .	1.0		26	44
•	1.5		5	
	2.0	Less than	1	60

To achieve a rapid precipitation of silver from solution, a large excess of iron in the form of parallel vertical steel rods 1 mm in diameter was placed in a column. A solution of 20% sodium chloride containing 100 ppm silver was passed down the column and the silver precipitated as a sponge on the surface of the iron and fell to the bottom of the column. The sponge was 15 analysed and shown to have a ratio of silver to iron of 75 to 1.

# BRIEF DESCRIPTION OF THE DRAWING

The drawing shows a flowsheet for the process. Concentrate or ore (1) is mixed counter-currently in vessel 10 with a strong chloride solution (2) and aerated with or without the presence of ionic copper as catalyst. The solids (3) are separated from solution (4). Solids 3 are removed for subsequent leaching (8,9) before being removed as spent solids 12. The solution is passed to a column (5) packed with vertical steel or iron rods or other packing (not shown) which would allow easy passage of the silver powder to the bottom of the column. The solution (4) passes down the column (5) and silver precipitates on the surface of the packing elements and falls to the bottom. The precipitated silver from the bottom (6) of the column (5) may be removed by filtration or by other suitable means. The resultant high grade silver product 11 (95%+ in contrast to the prior art references)



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may be further up graded by simple methods. When iron or steel packing elements are used iron is liberated during the silver precipitation. However contaminated solution (7) is subjected to said subsequent leaches (8, 9) where the iron is precipitated leaving uncontaminated solution (2). In a continuous counter-current contacting operation it may be desirable to maintain in the last thickener or reactor a slight excess of chlorine gas to maintain a positive starch iodide test, so that any oxidisable material which is resistant to the air oxidation in the earlier stages ... may be leached. If gold recovery is desired, it would be necessary to ensure that the pH was raised above about 4 at least in some or all of the reactors or thickeners.

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The claims defining the invention are as follows:

1. A process for the recovery of silver from a silver bearing ore or concentrate which comprises:

- (a) forming a mixture of ore or concentrate and a strong electrolyte containing sufficient chloride ions to form a complex with the silver,
- (b) maintaining the mixture at a temperature up to the boiling point of the electrolyts,
- (c) maintaining the pH of the mixture above 2, whereby silver is taken into solution; and
- (d) contacting the solution with metallic iron or steel to precipitate the silver from the solution.
- .2. A process for the recovery of gold from gold bearing ore or concentrate which comprises:
- (a) forming a mixture of ore or concentrate and a strong electrolyte containing sufficient chloride ions to form a complex with the gold,
- (b) maintaining the mixture at a temperature up to the boiling point of the electrolyte,
- (c) maintaining the pH of the mixture above 4, whereby the gold is taken into solution; and
- (d) contacting the solution with a metal in the electrochemical series having a potential above that of the gold to precipitate the gold from the solution.
- 3. The process according to any one of claims 1 or 2 wherein an oxygen bearing gas is introduced into the said mixture.
- 4. The process according to any one of claims 1 to 3 wherein said mixture additionally contains ionic copper.
- 5. The process according to any one of the claims 1 to 4 wherein miorize ion or hypochlorize ion is added to said mixture.









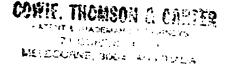


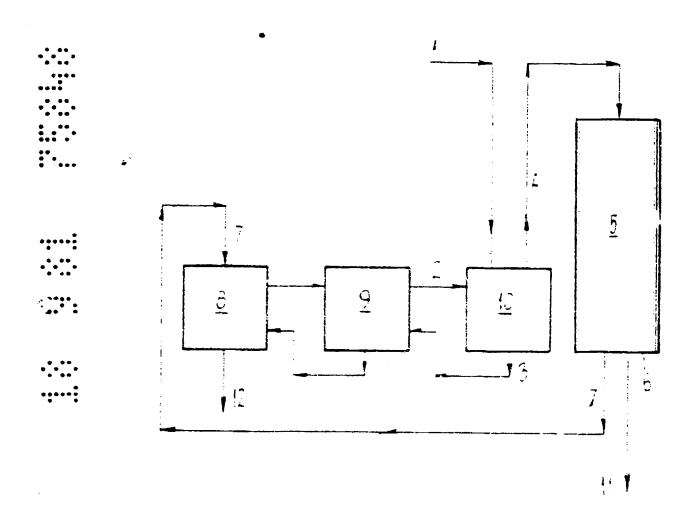
- 6. The process according to any one of claims 1 to 5 wherein said metal is metallic iron or steel.
- 7. A process according to any one of claims 1 to 6 wherein precipitation is carried out in a column containing a plurality of elongated iron or steel members.
- 8. The process according to claim 7 wherein said members are disposed generally parallel to each other.
- 9. The process according to either claim 7 or claim 8 wherein said members are orientated in a vertical direction.
- 10. The process according to claim 8 wherein said members are a packing of waste steel from lathe or other operation with a void size of greater than 5 mm.
- 11. The process of claim 1 wherein the dissolution of the silver is carried out in a contacting system and at least a part of the resultant silver contained in solution is precipitated in a separate vessel.
- 12. The process of claim 2 wherein the dissolution of the gold is carried out in a contacting system and at least a part of the resultant gold contained in solution is precipitated in a separate vessel.
- 13. The process according to either claims 11 or 12 wherein the contacting system is a counter-current system.
- 14. The process of any one of claims 11 to 13 wherein the solution resulting after precipitation is recycled to said counter-current contact solution.

- 15. A process for the recovery of silver and gold from a silver and gold bearing ore or concentrate which includes:
- (a) forming a mixture of ore or concentrate and a strong electrolyte containing sufficient chloride ions to form a complex with the silver and gold,
- (b) maintaining the mixture at a temperature up to the boiling point of the electrolyte,
- (c) maintaining the mixture at a pH sufficient to selectively take silver into solution,
- (d) contacting the solution with a metal having a potential above silver in the electrochemical series to thereby precipitate silver from the solution,
- (e) adjusting the pH of said solution to a level whereby gold is taken into said solution, and
- (f) contacting the solution with a metal having a potential above gold in the electrochemical series to precipitate gold from the solution.
- 16. A process for the recovery of silver and/or gold from a silver and/or gold bearing ore or concentrate substantially as hereinbefore described with reference to the examples and the accompanying drawing.

DATED this 3rd day of May, 1983 DEXTEC METALLURGICAL PTY. LTD.









# INTERNATIONAL SEARCH REPORT International Application No. | FOT/AU ST 00136

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